

Early diagenesis in biogenic carbonates of temperate and shoal waters (Cadiz Bay and adjacent continental shelf)

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Received October 1997. Accepted April 1998.

ABSTRACT

Because of the chemical reactivity of biogenic carbonates in shallow waters, there is increasing interest in those early diagenesis processes that imply an alteration or variation of the composition of original material. This paper presents the preliminary results of a study concerning the compositional variations that have taken place in the skeletons or skeletal remains of bryozoans and echinoids. This variation, which includes an aragonite-calcite transformation, has been checked by means of the Rietveld method, using the Fullprof program. This transformation is caused by an *in situ* dissolution-recrystallisation process, due to aragonite's metastability. Moreover, the presence of specific authigenic minerals helps to delimit early diagenetic processes, which are, in turn, indicative of the path and the extension of the diagenetic reactions that take place in the sediment column.

Key words: Biogenic carbonate, dissolution-recrystallisation process, authigenic minerals, diagenetic environment.

RESUMEN

Diagénesis temprana en carbonatos biogénicos de aguas someras y templadas (bahía de Cádiz y plataforma continental adyacente)

Debido a que los carbonatos biogénicos de aguas someras son químicamente muy reactivos, existe cada vez mayor interés por conocer los procesos de diagénesis temprana que conllevan una alteración o modificación de la composición del material original. En este trabajo se presentan los resultados iniciales sobre las variaciones de composición que han tenido lugar en los caparazones o restos del esqueleto de equinodermos y briozoos. Esa variación, incluida la transformación aragonito-calcita, ha sido chequeada mediante el método Rietveld, programa Fullprof. Dicha transformación ocurre por un proceso de disolución-recristalización debida a la metaestabilidad del aragonito. Además, la presencia de una asociación de minerales neoformados implica procesos diagenéticos tempranos indicativos de las reacciones que tienen lugar en la columna del sedimento.

Palabras clave: Carbonatos biogénicos, neomorfismo, minerales autigénicos, ambientes diagenéticos.

INTRODUCTION

Although there are differences in the diagenetic behaviour of temperate and tropical waters' biogenic carbonates, as shown in the former by a lower carbonate saturation level (among other factors), this, in turn, leads to few or rare cementation processes. Nevertheless cements of aragonite or calcite composition with high magnesium content have been linked with sulphate reduction processes, and more commonly in environments where evaporation causes an increase in carbonate concentration (Reeckmann, 1988). Despite these differences, there are also some similarities, due to the nature of the biogenic carbonates that make up the skeletal remains of organisms. The mineralogy of these sediments basically corresponds to chemically metastable phases (aragonite and magnesian calcites), which are not unique systems; rather, the carbonate minerals at low temperature show solid solutions, where Mg and Sr are important trace elements. The existence of these characteristics (chemical-mineralogical) must be considered when dealing with the physical, chemical and biological factors that cause the post-mortem changes in this material and during its diagenesis, since these processes may alter the original compositions and therefore render them useless as palaeoenvironmental indicators (Walls, Ragland and Crisp, 1977).

Most of the research has been directed at the alterations undergone by dissolution of the carbonate sediments in deep waters; recently, further evidence has been offered for the importance of early diagenesis processes in carbonate shoal water sediments (Walter and Burton 1990; Walter *et al.*, 1993). These are chemically more reactive, and their textural and compositional variations are produced prior to deep burial, therefore underlining the importance of determining the rate and the early diagenetic process sequence that occur in marine and meteoric environments.

In the present paper, the preliminary results of a study on biogenic carbonate reactivity that has been subjected to a phase transformation process, in particular aragonite-calcite, are discussed. This transformation (known as neomorphism) is caused by an *in situ* dissolution-precipitation process, due to aragonite's metastability (Rehman *et al.*, 1994), apparently without developing a significant porosity, but with grain-size increase. In the determination of the path and the extension of the diagenetic

reaction, several factors are involved (e.g. saturation state, skeletal structure, climate, and specific authigenic minerals) which effectively delimit different diagenetic environments. This work will then be complemented by a study concerning global sediment and diagenetic fluid composition, to establish an adequate palaeoenvironmental characterisation.

MATERIALS AND METHODS

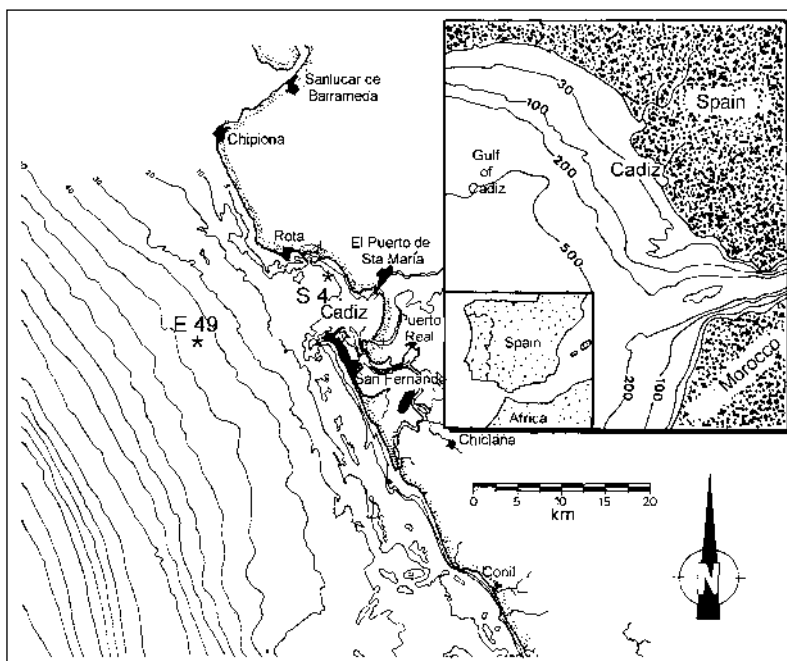
Samples corresponding to skeletons and skeletal remains of bryozoans and echinoids were used. These samples are part of the extracted sediments of two piston cores of different lengths (75 cm and 120 cm), taken from the outer part of Cadiz Bay and the adjacent inner continental shelf (figure 1).

The study involved granulometric, mineralogical and geochemical analysis of these samples.

In the granulometric analysis, the usual procedure was used for the separation of the fine and coarse fractions, and the variation of their different components every 10 cm, for each of the cores. Likewise, determination of the carbonate in the total fraction was performed on one of the cores by means of an acid-base titration; the study furthermore comprised an analysis of the nature of the skeletons and skeletal remains through observation and grain separation with binocular microscope at each interval of the sand fraction.

The mineralogical and geochemical analyses were based on phase identification from x-ray diffraction profiles and Scanning Electron Microscope (SEM) observations. Detailed study of the aragonite-calcite mineralogical transformation was based on the analysis of the powder diffraction patterns by means of the Rietveld method (Rietveld 1967, 1969), using the Fullprof program (Rodríguez-Carvajal, Anne and Pannetier, 1987). This technique has become increasingly useful as a tool for the analysis of such patterns. In the analysis, a maximum probability fit was used rather than the integrated intensity of the diffraction peaks between the observed diffraction profile and a calculated diffraction pattern, using structural parameters for each component (aragonite and calcite); likewise a pseudo-Voigt function (Thompson-Cox-Hastings) was used in the profile fit; the background was modelled using cubic splines. The structural variables used in the fit were: spatial group, atomic

Figure 1. Bathymetric map of the study area and geographic distribution of samples (after Lobo, 1995)



positions and cell parameters. This technique enabled us to make a quantitative analysis of each of the samples without having to calculate the structural factors since the derived scale factors for each of the components determines their relative abundance.

The SEM observations correspond only to the bryozoans, and some samples were polished and etched with diluted acid.

RESULTS

Granulometric analysis of the cores (figures 2 and 3) shows the variation of their different components. In general, three levels can be distinguished in core E-49: the top level corresponds to the first 30 cm in the core and presents the higher mud content and a content in carbonates of 26 %. The intermediate level (30-41 cm) consists predominantly of muddy sand and the content in carbonates is 25 %. In the lower level (41-75 cm), quartz-rich sand predominates, with a lower carbonate content (18 %). The analysis of core S-4, likewise, showed three different levels: the superficial level corresponds to the first 48 cm in the core and is composed of fine sand; the intermediate level (48-97 cm) composed of medium and coarse sand with bioclasts; and the deepest level (97-120 cm) composed of coarse sand with bivalve shells.

The MgCO_3 content of the magnesian calcites was estimated by the variation in the unit cell parameters

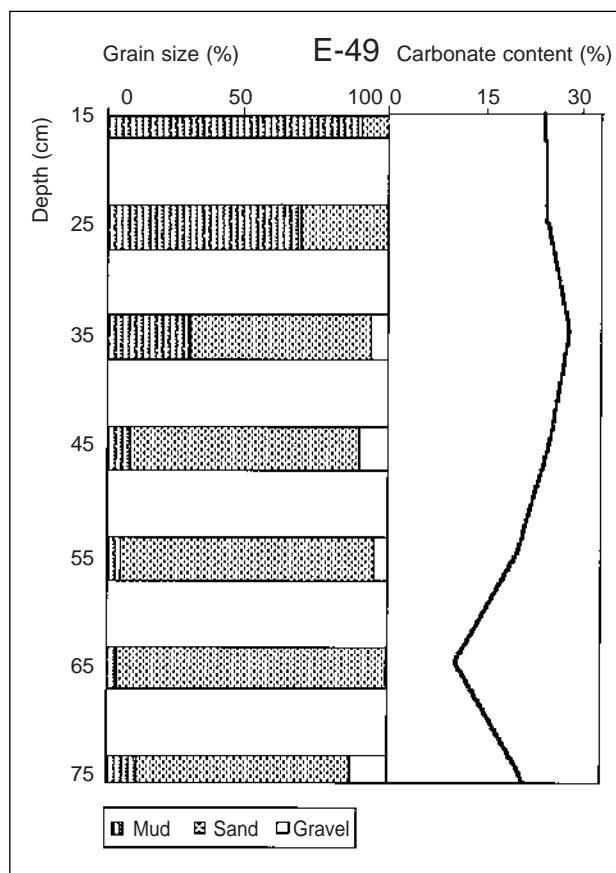


Figure 2. Granulometric analysis and variation in the carbonate content of core E-49

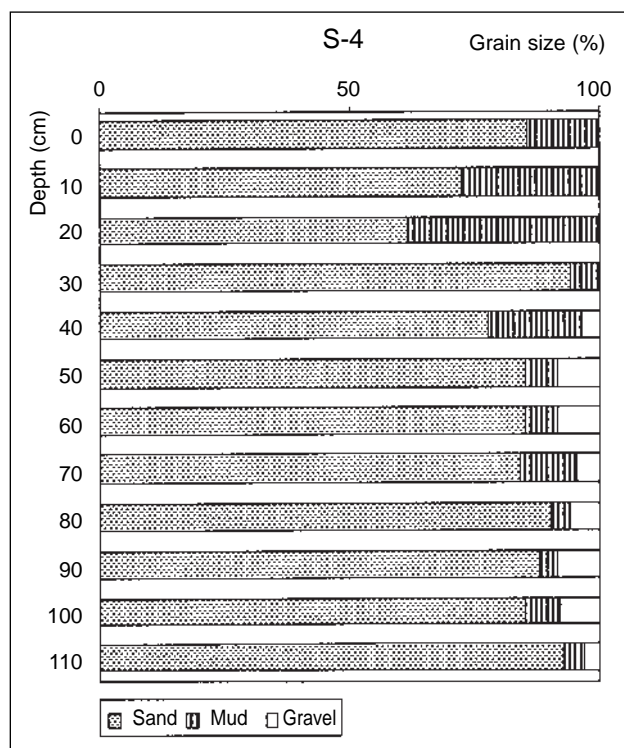


Figure 3. Granulometric analysis of core S-4

versus such content (Goldsmith, Graf and Heard, 1961; Bischoff, Bishop and Mackenzie, 1983). These studies, carried out under conditions of high pressure and temperature, yield some standard values of these uniform and constant parameters, which may be used to estimate the composition of inorganic and biogenic calcites. These values are the result of a linear variation of the axial relation c/a with the Mg content of between pure dolomite and calcite.

Echinoids

The echinoid samples belong to core E-49 and correspond to broken skeletal fragments and the

results of the X-ray diffraction are shown in table I and figure 4. The skeletal remains of these organisms are predominantly magnesian calcites because of the presence, in the diffraction profile, of the maximum intensity peak corresponding to a reflection of 104 ($2\theta = 29.57^\circ$). However, aragonite was detected in sample E-49-4 (45 cm depth) by the presence of its characteristic reflections ($2\theta = 26.02^\circ$ and $2\theta = 27.01^\circ$ respectively). This component diminishes in deeper samples, which can be interpreted as a dissolution process favouring the stable phase (calcite), the content of which increases with depth. In the case of samples E-49-6 and E-49-5, they are exclusively magnesian calcites; it should be noted, however, that the reflection intensity of 104 is less in the second and also the area corresponding to the profile background determined by the Fullprof program is larger in the latter (table I). The area can be calculated because the Fullprof program makes it possible to separate the part of the diffraction profile that corresponds to the crystalline part of the sample (presence of reflections) from the one that may be amorphous or scarce crystalline (presence of background). Thus, the global behaviour of the sequence can be interpreted as a dissolution process (lower intensity) and precipitation (larger area background) of the calcitic components in the shallower samples. Subsequently, there is a precipitation of aragonite (E-49-4) which undergoes a noticeable alteration process between depths of 55-65 cm, as it changes from 18 % to 6.5 %.

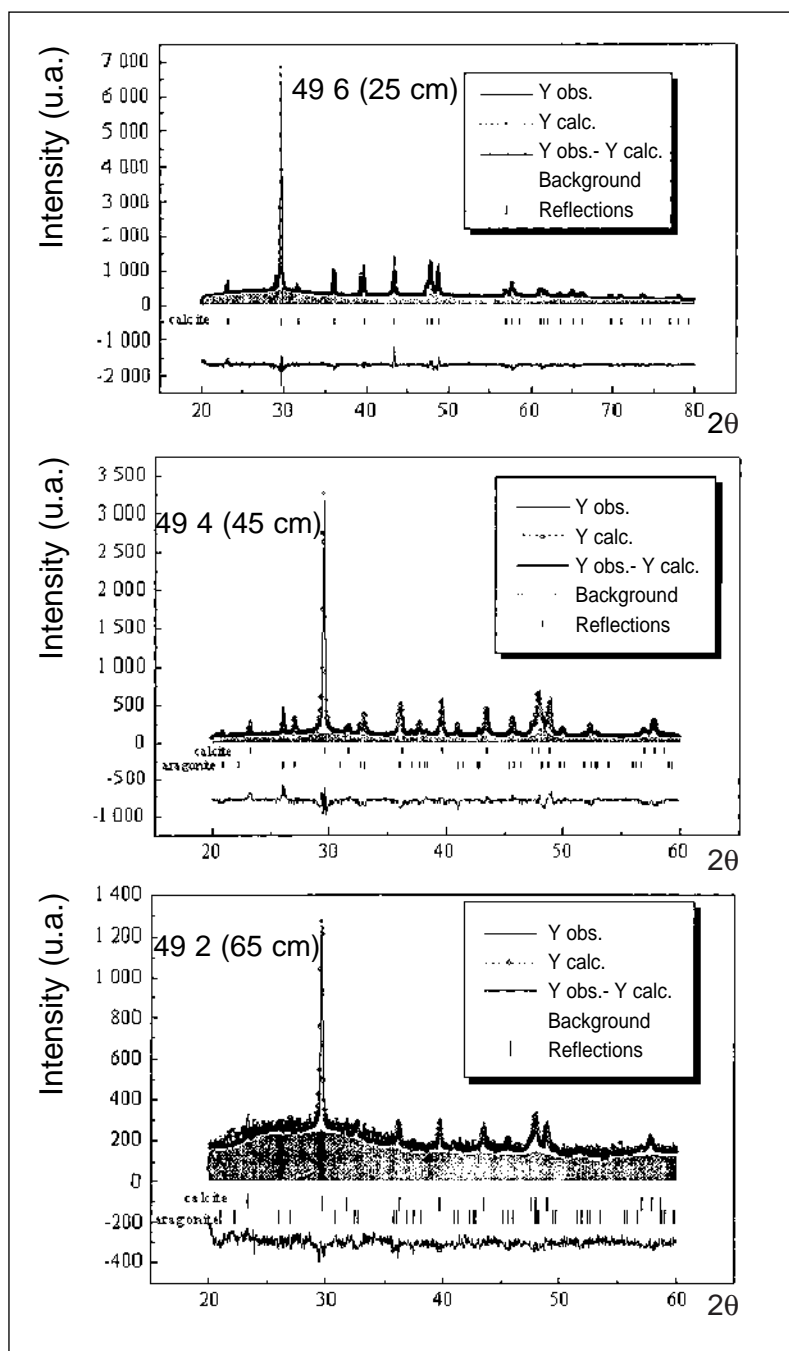
Bryozoans

The bryozoan samples belong to core S-4 and correspond to broken skeletal fragments, which made their identification and classification diffi-

Table I. Calcite and aragonite contents of echinoid samples (E 49)

Sample	Echinoids				
	49-6 (25 cm)	49-5 (35 cm)	49-4 (45 cm)	49-3 (55 cm)	49-2 (65 cm)
Magnesian calcite	100 %	100 %	80 %	82 %	93.5 %
(MgCO_3)	(8 %)	(8 %)	(3.5 %)	(10 %)	(8 %)
Background (area)	(14 094 ua)	(17 405 ua)			
Aragonite	–	–	20 %	18 %	6.5 %

Figure 4. Diffraction profile-fitted models according to the Rietveld method, corresponding to echinoid skeletons or skeletal remains at different depths. The continuous line shows the experimental data, the discontinuous line and open circle refer to the fitted model (calculated) and the lower continuous line shows the difference between the observed and the calculated data. The dark area corresponds to the background of the model



cults. Two populations (A and B) showing texturally different features have, however, been separated, and both belong to the order cheilostomata.

The results of the x-ray diffraction of population A are exclusively composed of magnesian calcites. The skeletal remains of population B, largely of aragonite and magnesian calcite composition, are shown in table II. Quartz is present at all depths, and is found in voids and pores of the skeletal fragments as a detrital mineral. The tendency of car-

Table II. Calcite and aragonite contents of bryozoan (B) samples (S-4)

Sample	Bryozoans (B)		
	S-4 (10 cm)	S-4 (60 cm)	S-4 (110 cm)
Magnesian calcite	52 %	57 %	59 %
(MgCO ₃)	(9 %)	(8 %)	(8 %)
Aragonite	48 %	43 %	41 %

bonate minerals is the opposite: whereas magnesian calcite increases its value with depth, aragonite diminishes. Therefore, there is a neomorphic aragonite-calcite transformation process, which may be due to a dissolution-recrystallization process, able to provoke a complete mineralogical change in the evolution of the sample's composition. The quantification of each of the phases was used to establish the kinetic transformation process that took place in the core, as shown in figure 5.

Likewise, the transformation process has been confirmed by SEM. Figure 6 shows the skeletal central walls (a) and three-layered microstructure (b) that indicate the inner foliated calcite between two layers affected by an early diagenetic process, which can be deduced from the existence of an infilling of sparry calcite (arrow, rhombohedral angle 46°).

Moreover, there is an authigenic mineralogical association: ferroan magnesium carbonate, glauconite and sedimentary iron sulphide, which presents a framboidal form. This association is found in

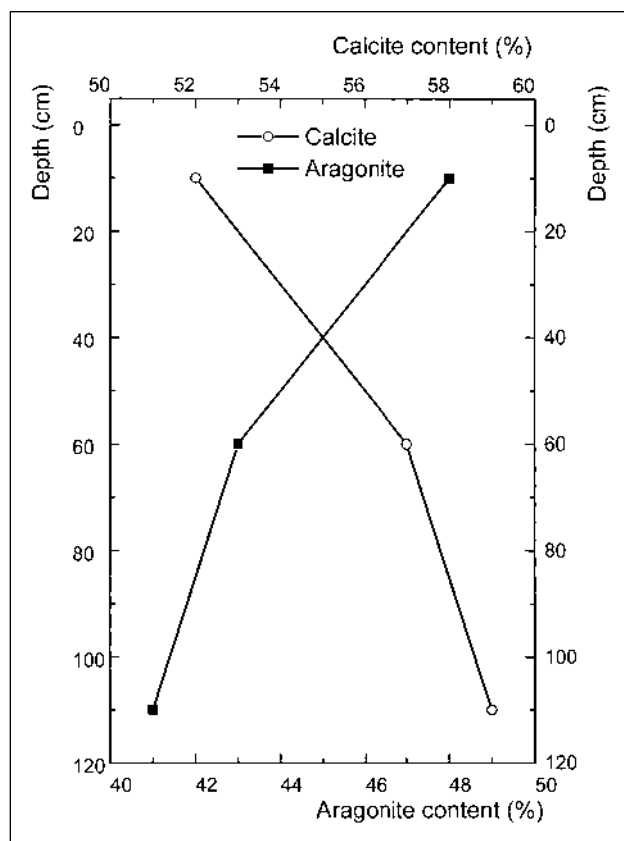


Figure 5. Variation in the aragonite and calcite contents with depth. The selected samples correspond to bryozoan skeletons (population B) or skeletal remains of core S-4

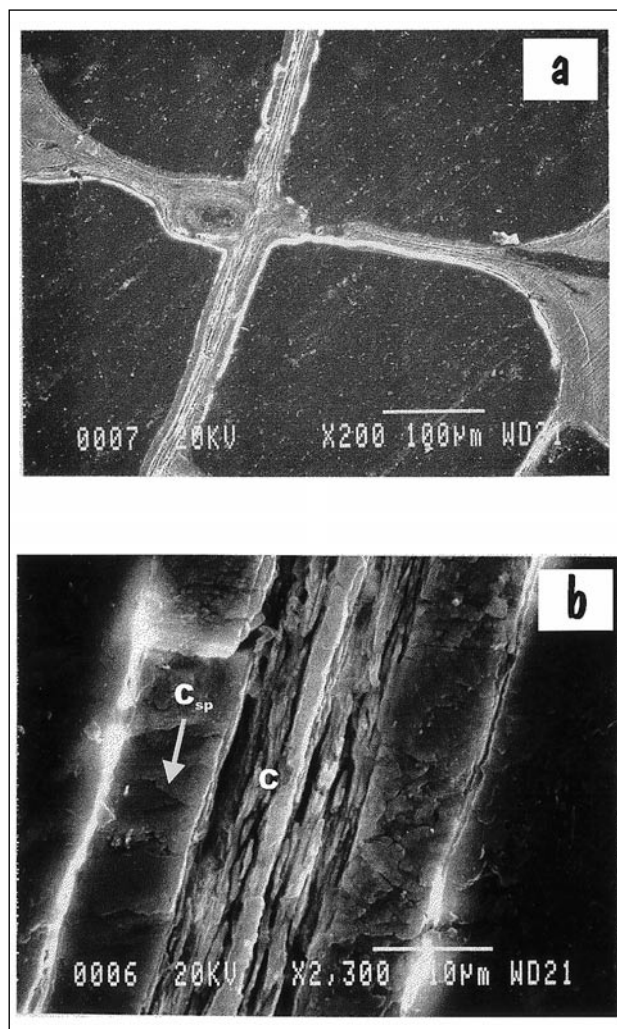


Figure 6. SEM photomicrographs of polished and etched samples of bryozoans. (a): General views showing the skeletal fragments. (b): Detailed views of the inner foliated calcite (C) and the sparry calcite (Csp) infilling the diagenetically altered layer

both bryozoan populations (A and B), being more abundant in B because of smaller voids and pores, and varies with depth. At 60 cm, the characteristic minerals are glauconite and ferroan magnesium carbonate (figure 7c), whereas iron sulphide (figure 7a) appears mostly at a depth of 110 cm, possibly presenting cubo-octahedron morphology (figure 7b). The identification of carbonate and iron sulphide is based on the distinctive EDX spectrum.

According to Berner (1981), this association determines different anoxic diagenetic environments: non-sulphidic post-oxic environments (sub-oxic), delimited by glauconite and carbonate, and sulphidic environments, delimited by iron sulphide. The latter occurs when the diagenetic sequence has

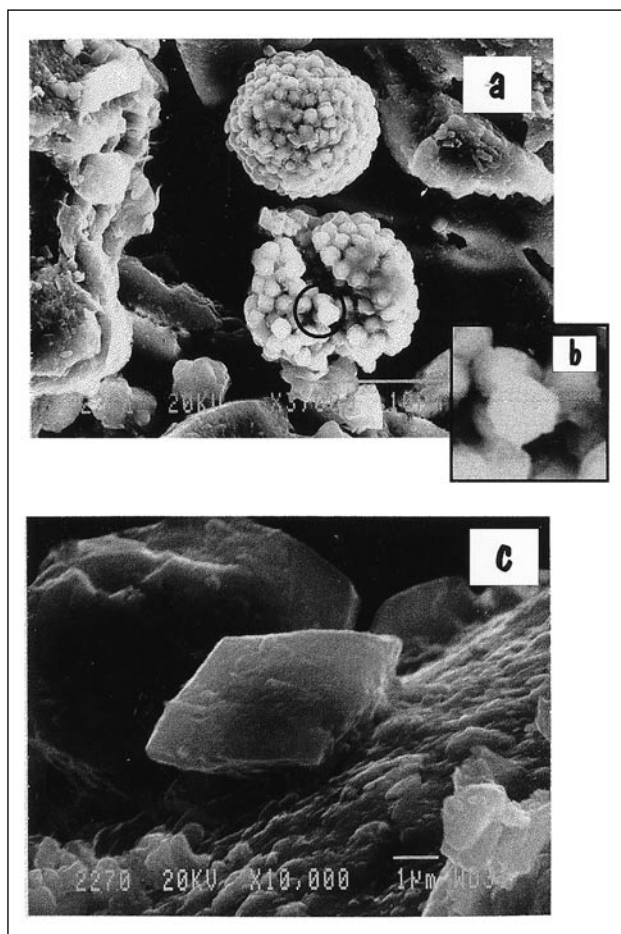


Figure 7. SEM photomicrographs of authigenic minerals. (a): framboidal iron sulphide (depth 110 cm); (b): detailed view from (a); (c): ferroan magnesium carbonate (depth 60 cm)

reached the stage at which the bacterial reduction of dissolved sulphate takes place, with the production of H_2S and HS^- . The sulphate-reduction process is indicated by the analysis of pore water from previous studies performed in the same area (Gómez-Parra and Forja, 1994). The subsequent reaction (H_2S + goethite) at pH 5 makes possible the formation of framboidal iron sulphide and the cubo-octahedron morphology, which in certain experiments (Wang and Morse, 1996) was controlled by the degree of supersaturation of the growth solution.

DISCUSSION

Based on the proposed methodology, the present paper has identified and quantified the mineral phases that make up the skeletons or skeletal

remains of certain organisms: echinoids and bryozoans.

Likewise, the study shows the depth variations for each of the components of these mineral phases, which has made it possible to establish the kinetics of the aragonite-calcite transformation process for sediments in temperate and shoal water in this geographic area, and a specific mineralogical association: ferroan magnesium carbonate, glauconite and iron sulphide, demonstrating the possibility of different diagenetic environments. In our opinion, the present study should form part of a global project (involving sediment composition and diagenetic fluid) to produce an adequate palaeoenvironmental interpretation.

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